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- (54) **OSMOTIC ENERGY CONVERSION WITH MXENE LAMELLAR MEMBRANE-BASED SYSTEM AND METHOD**
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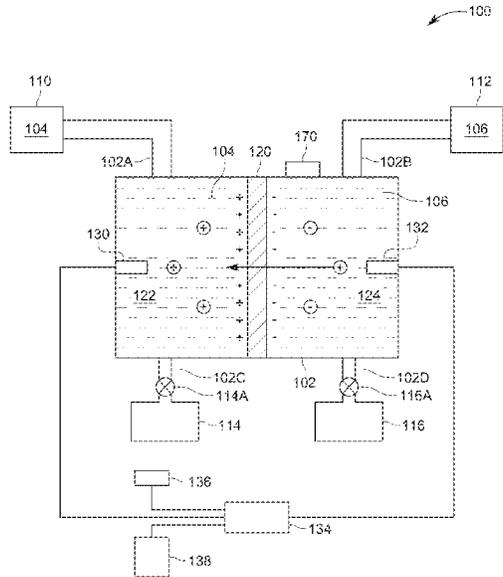
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(57) **ABSTRACT**

An osmotic energy conversion system includes a housing having a first inlet and a second inlet, an MXene lamellar membrane located inside the housing and configured to divide the housing into a first chamber and a second chamber, and first and second electrodes placed in the first and second chambers, respectively, and configured to collect electrical energy generated by a salinity-gradient formed by first and second liquids across the MXene lamellar membrane. The first chamber is configured to receive the first liquid at the first inlet and the second chamber is configured to receive the second liquid at the second inlet. The first liquid has a salinity lower than the second liquid, and the MXene lamellar membrane includes plural nanosheets of MXene stacked on top of each other.

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**20 Claims, 20 Drawing Sheets**



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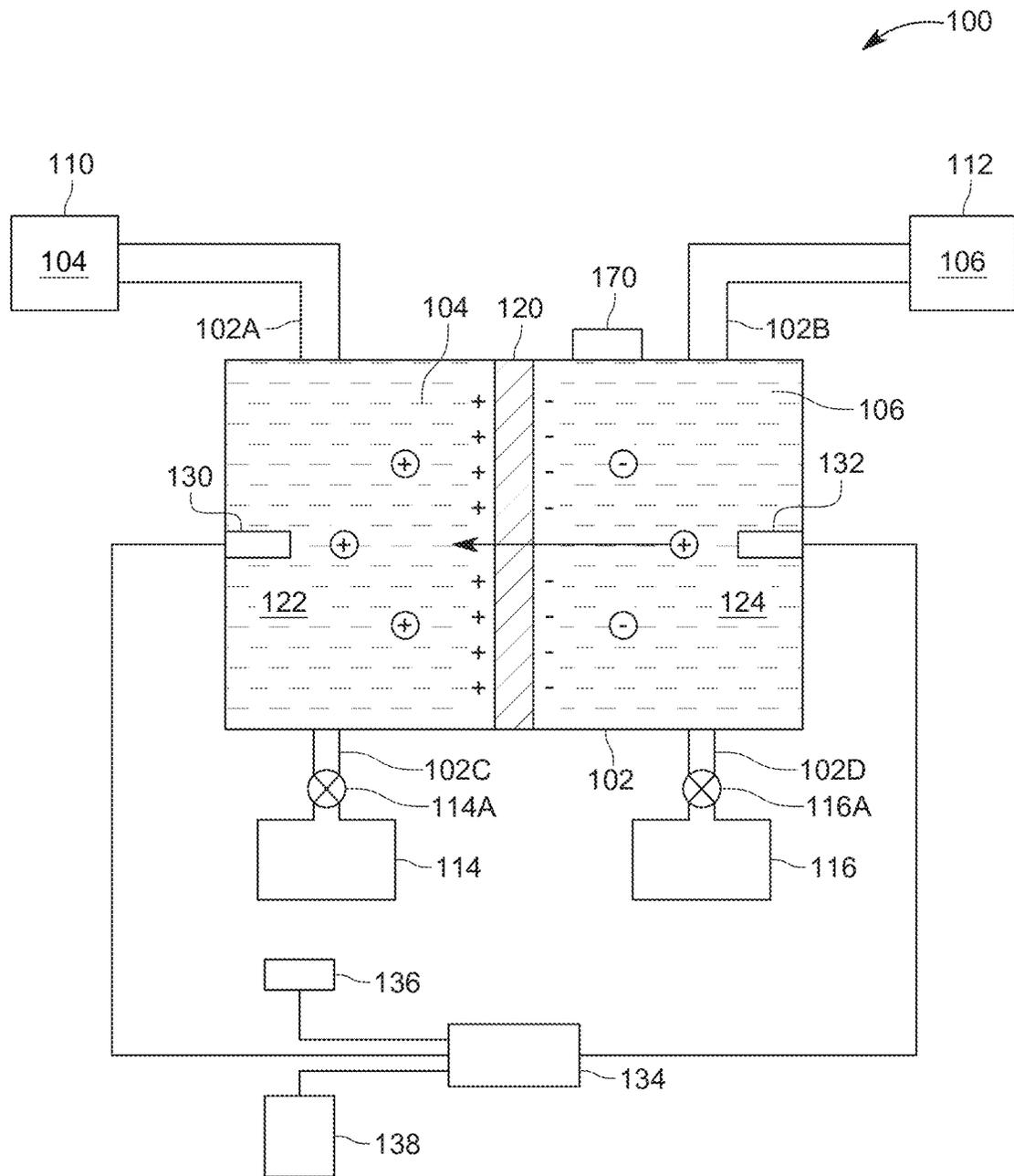


FIG. 1

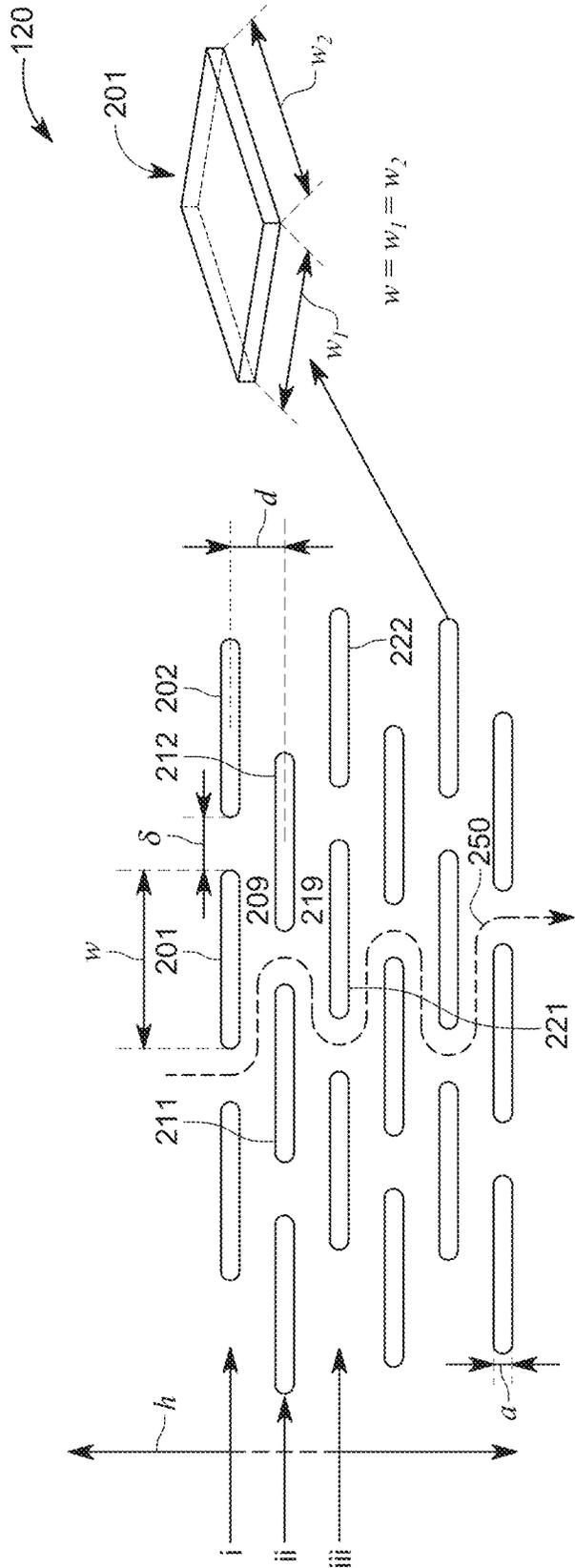


FIG. 2A



FIG. 2B

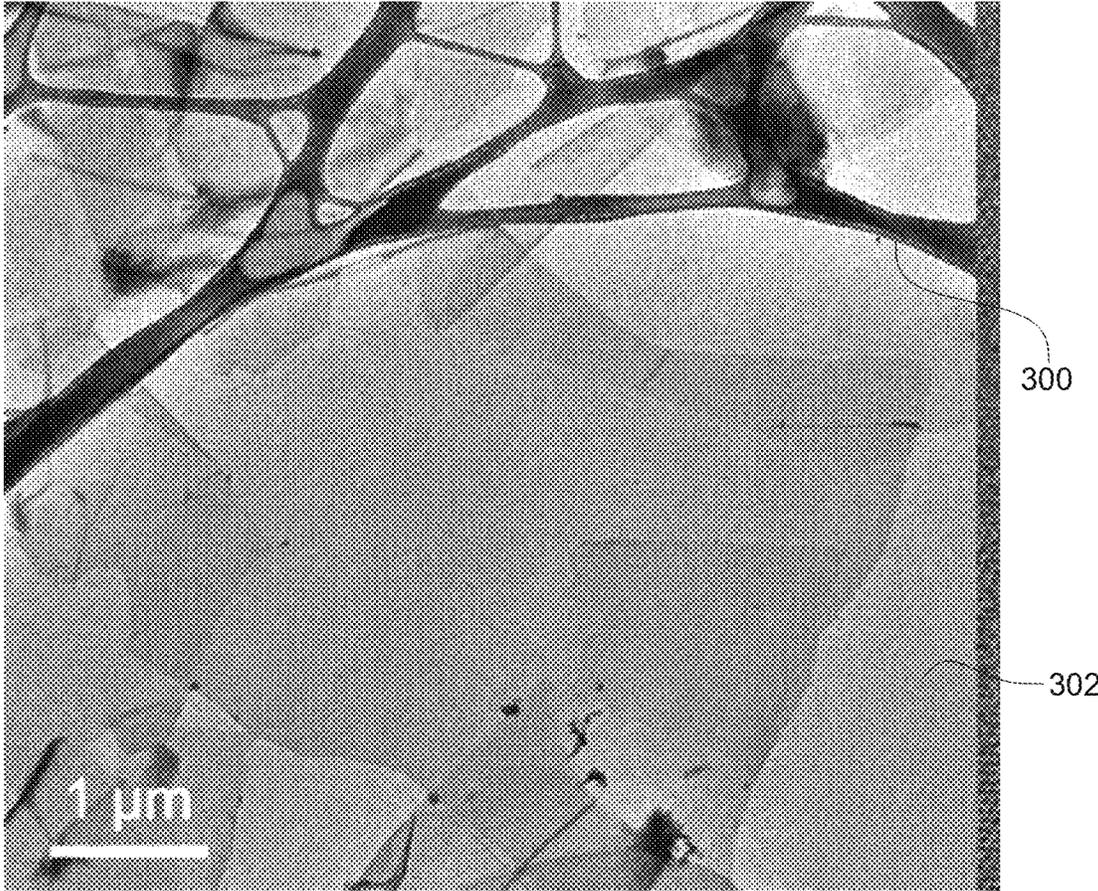


FIG. 3A

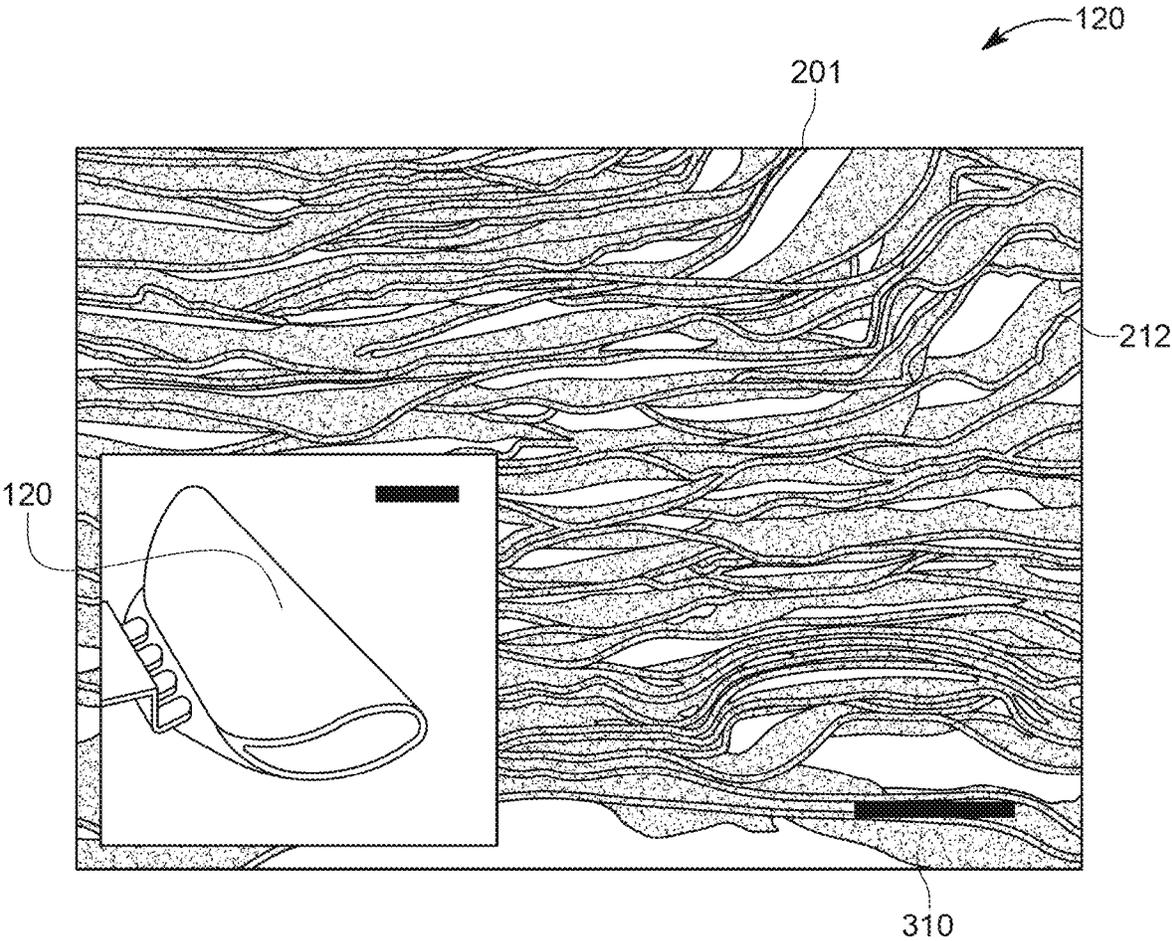


FIG. 3B

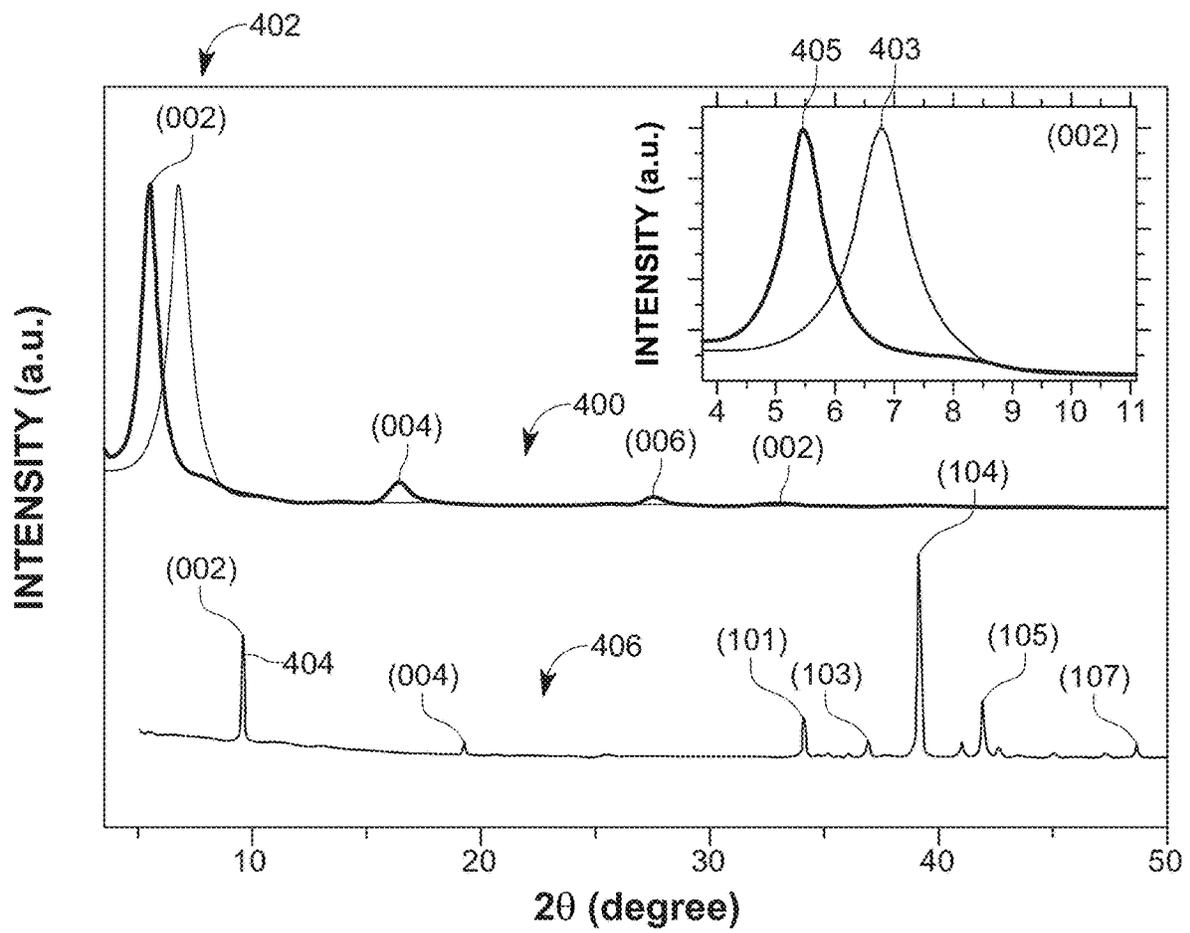


FIG. 4A

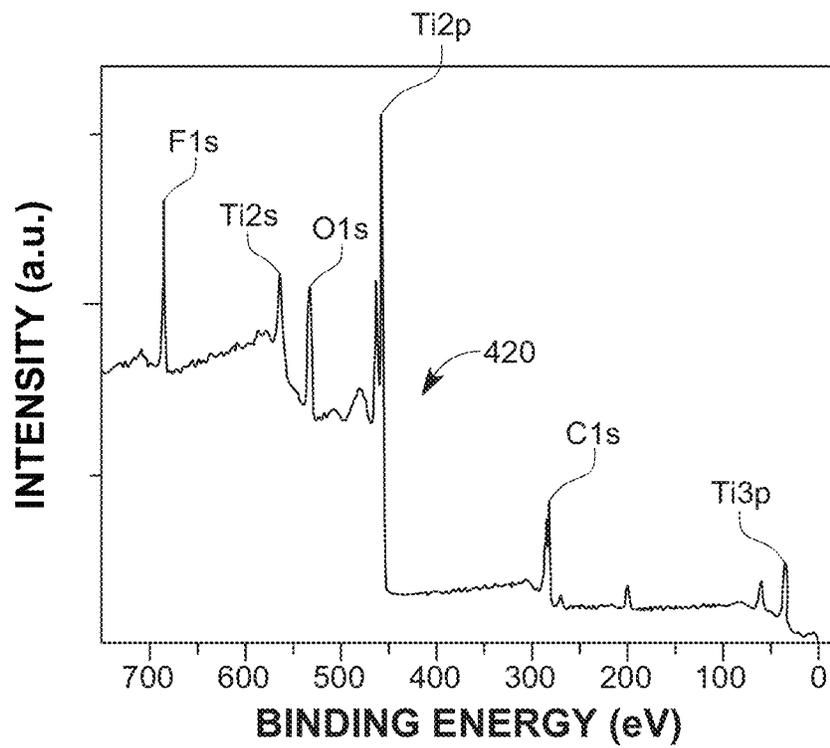


FIG. 4B

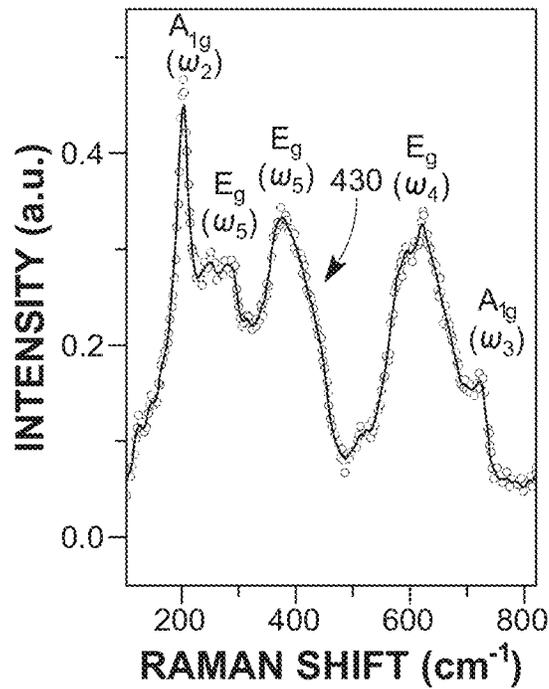


FIG. 4C

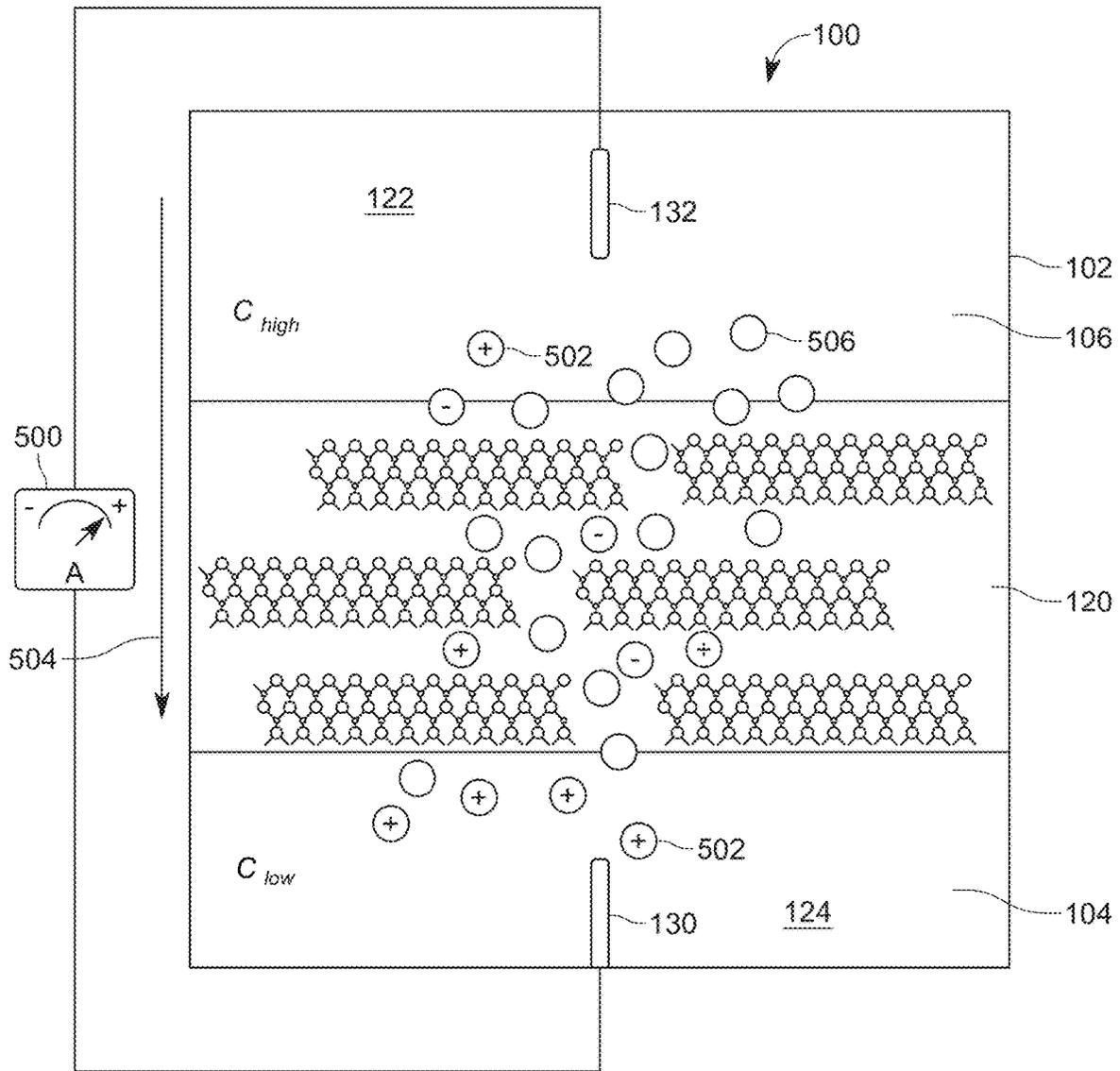


FIG. 5A

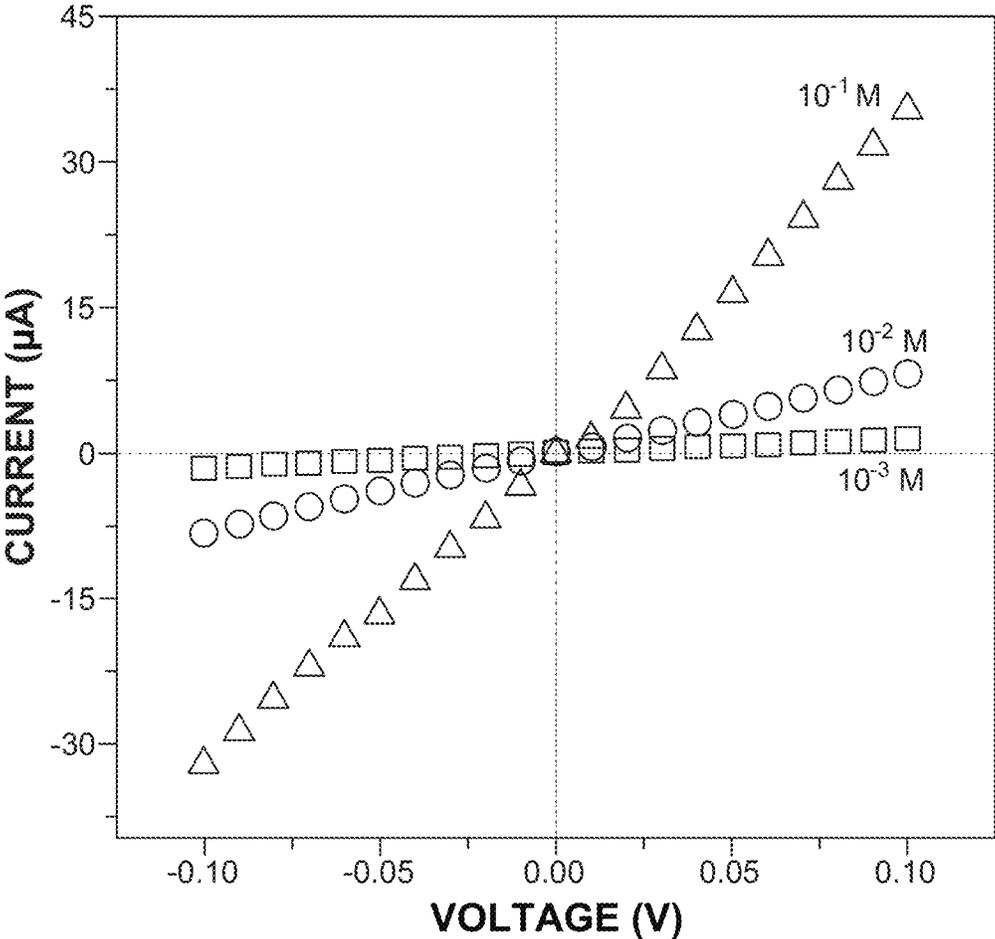


FIG. 5B

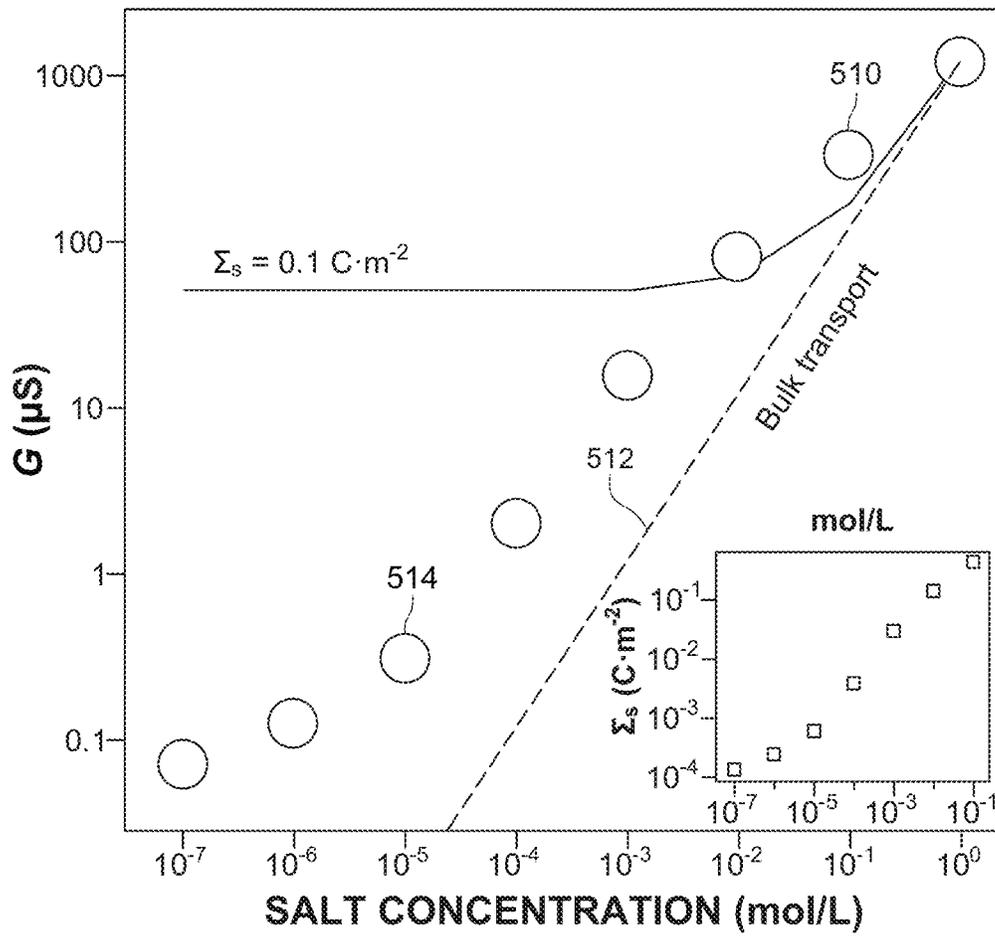


FIG. 5C

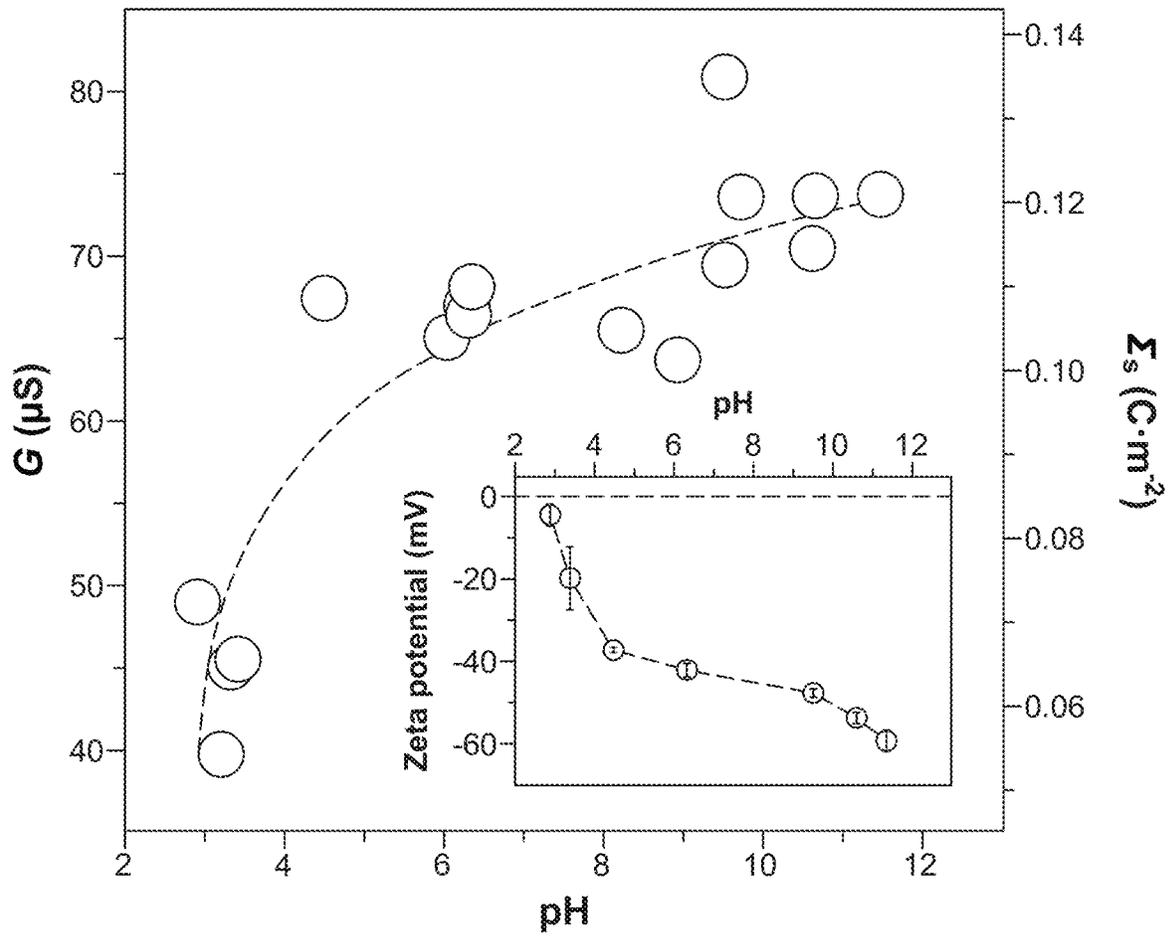


FIG. 5D

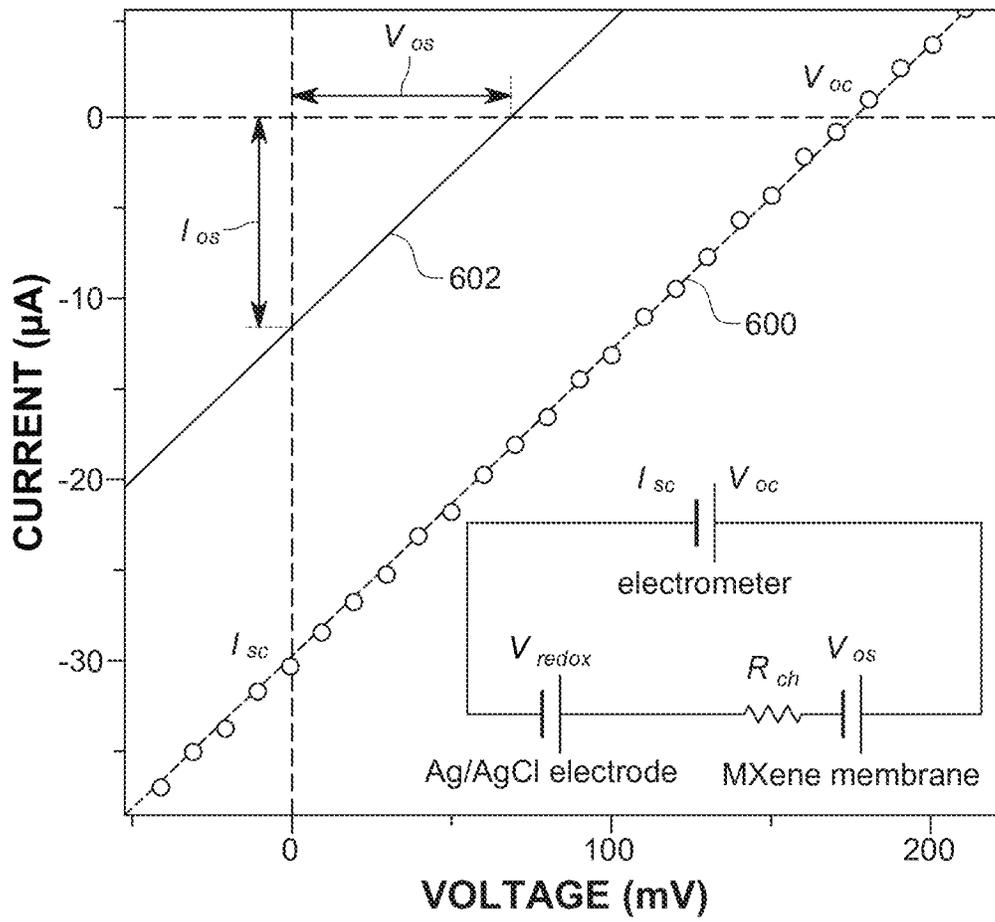


FIG. 6A

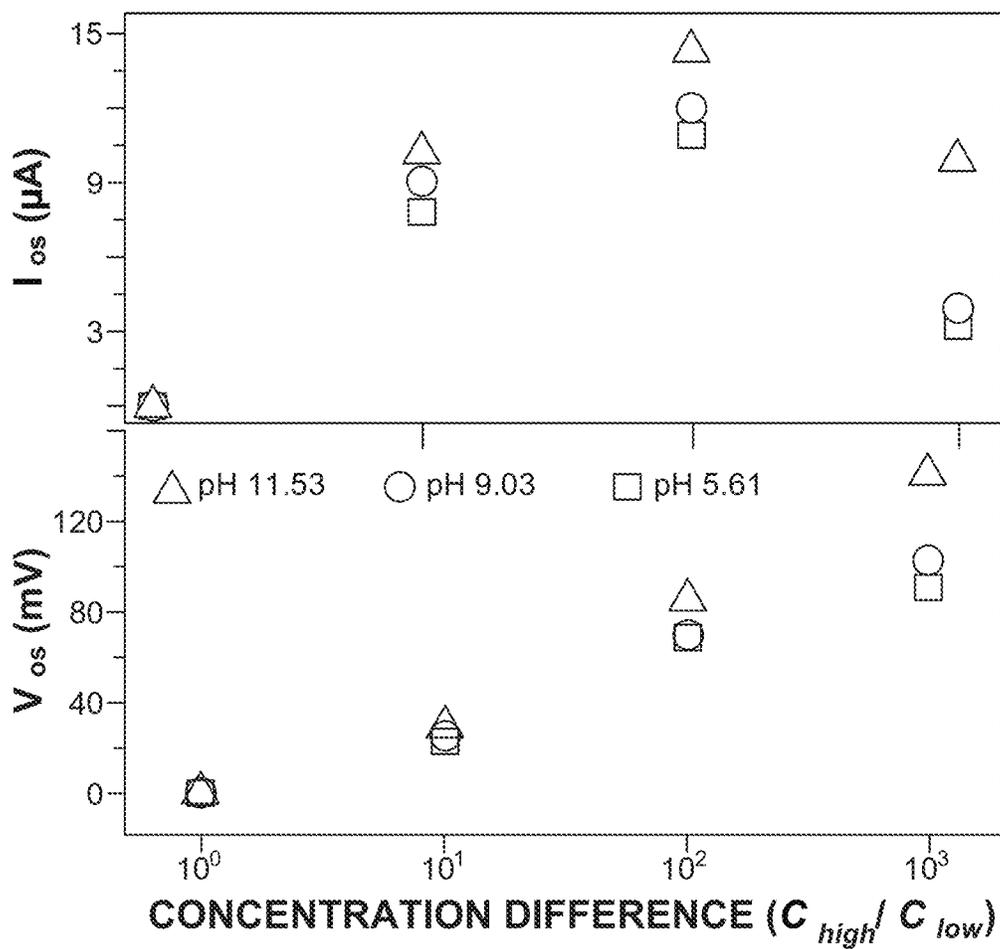


FIG. 6B

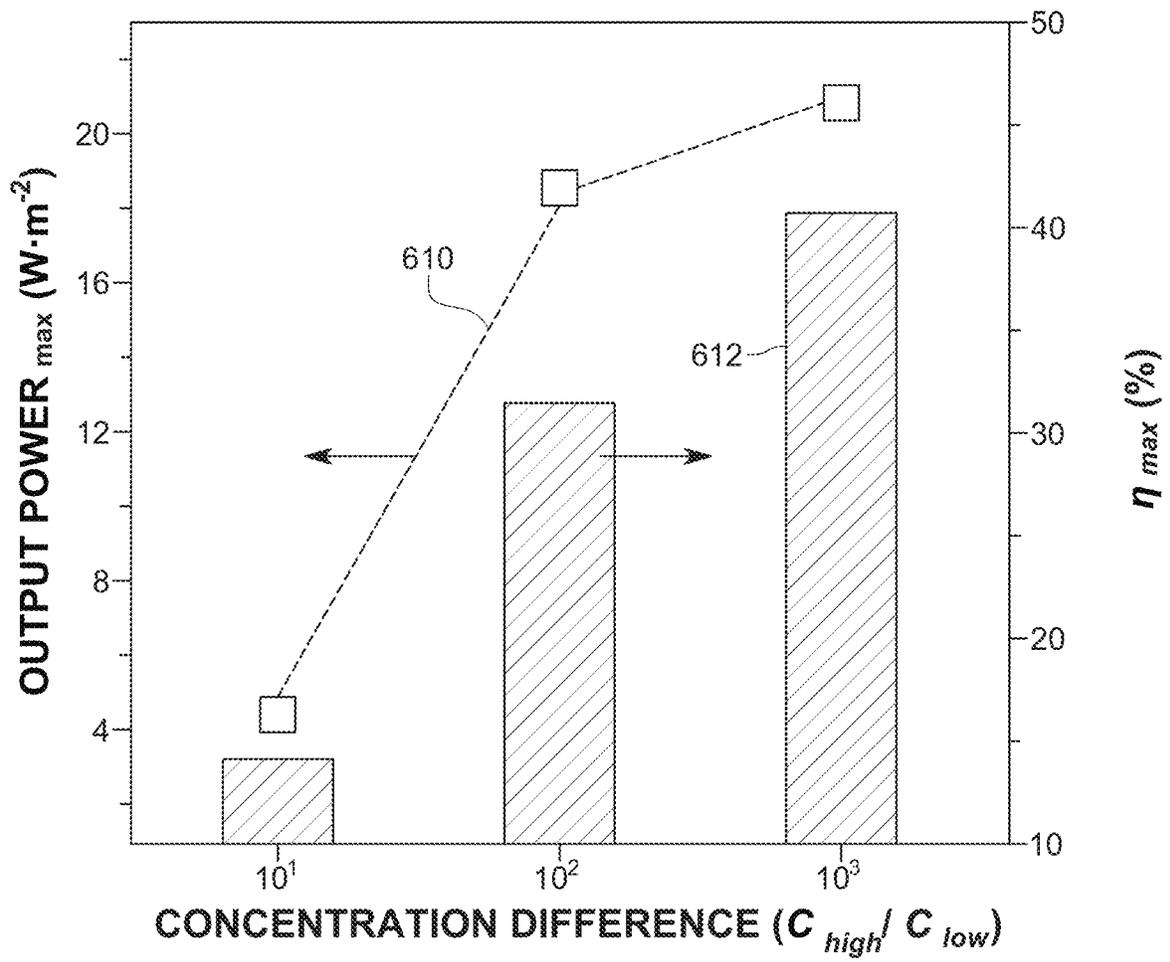


FIG. 6C

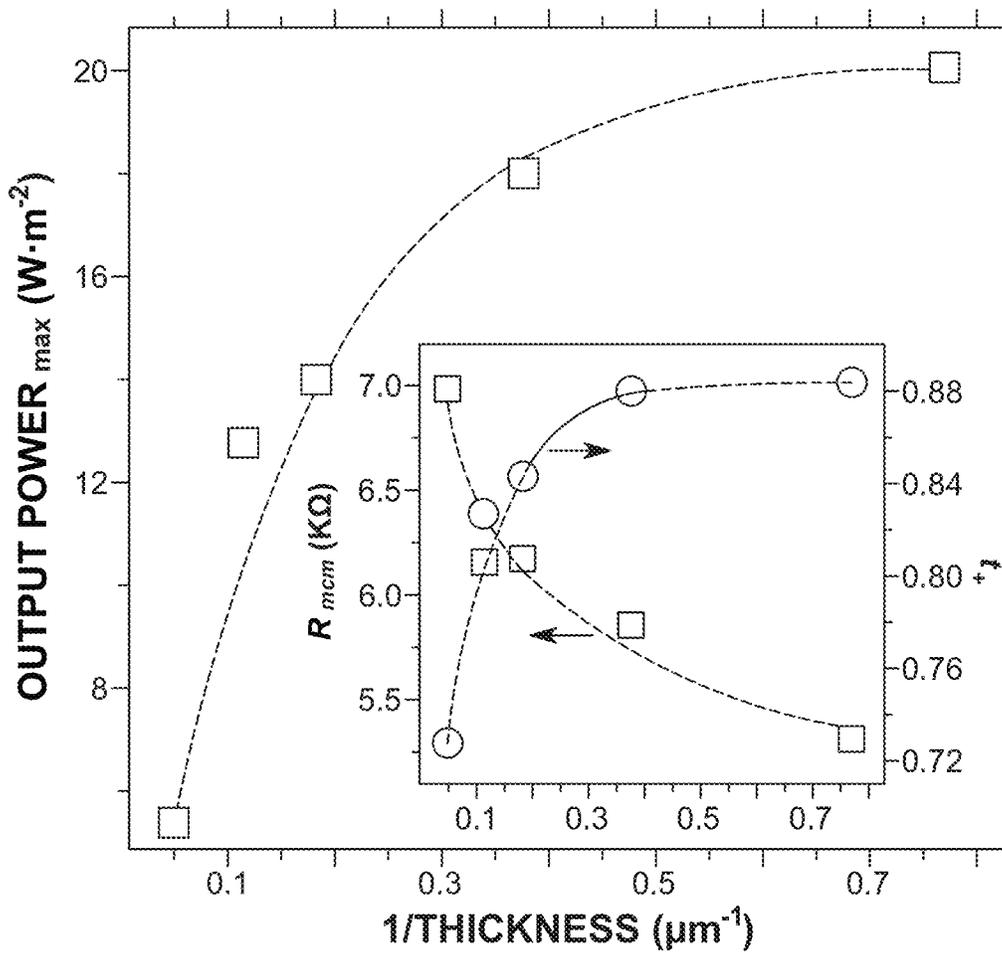


FIG. 6D

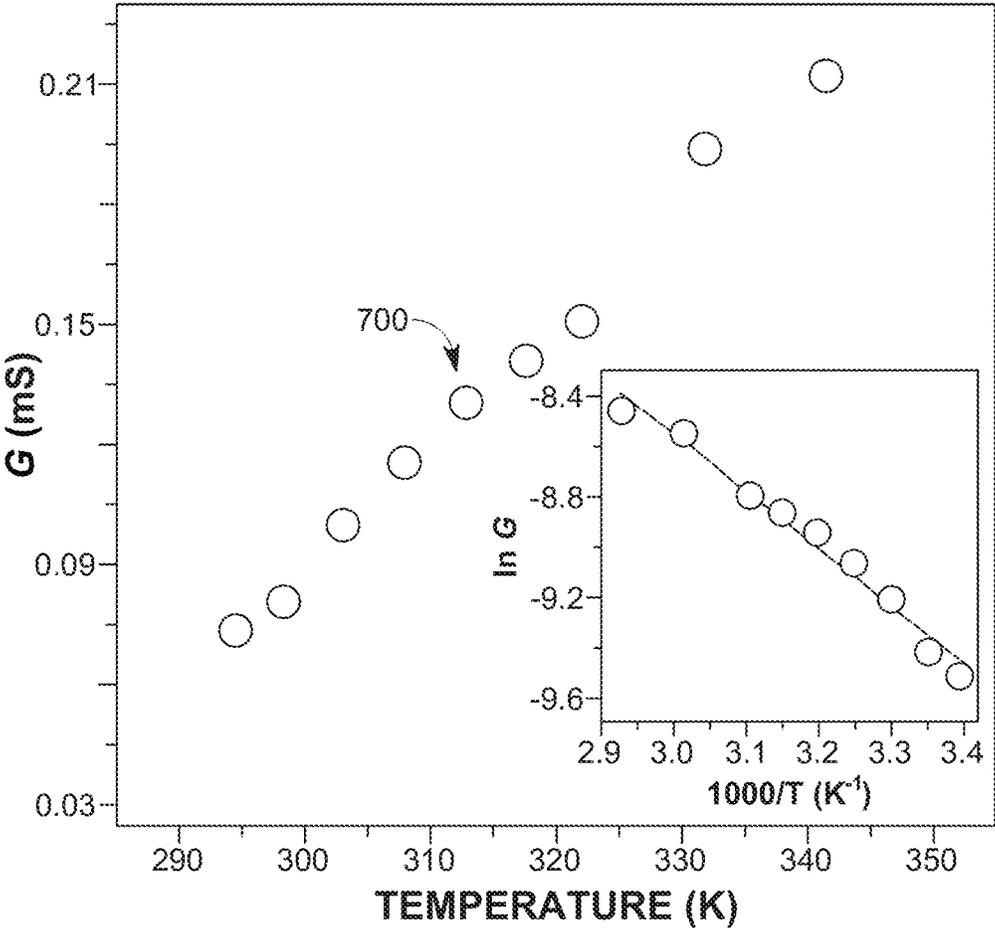


FIG. 7A

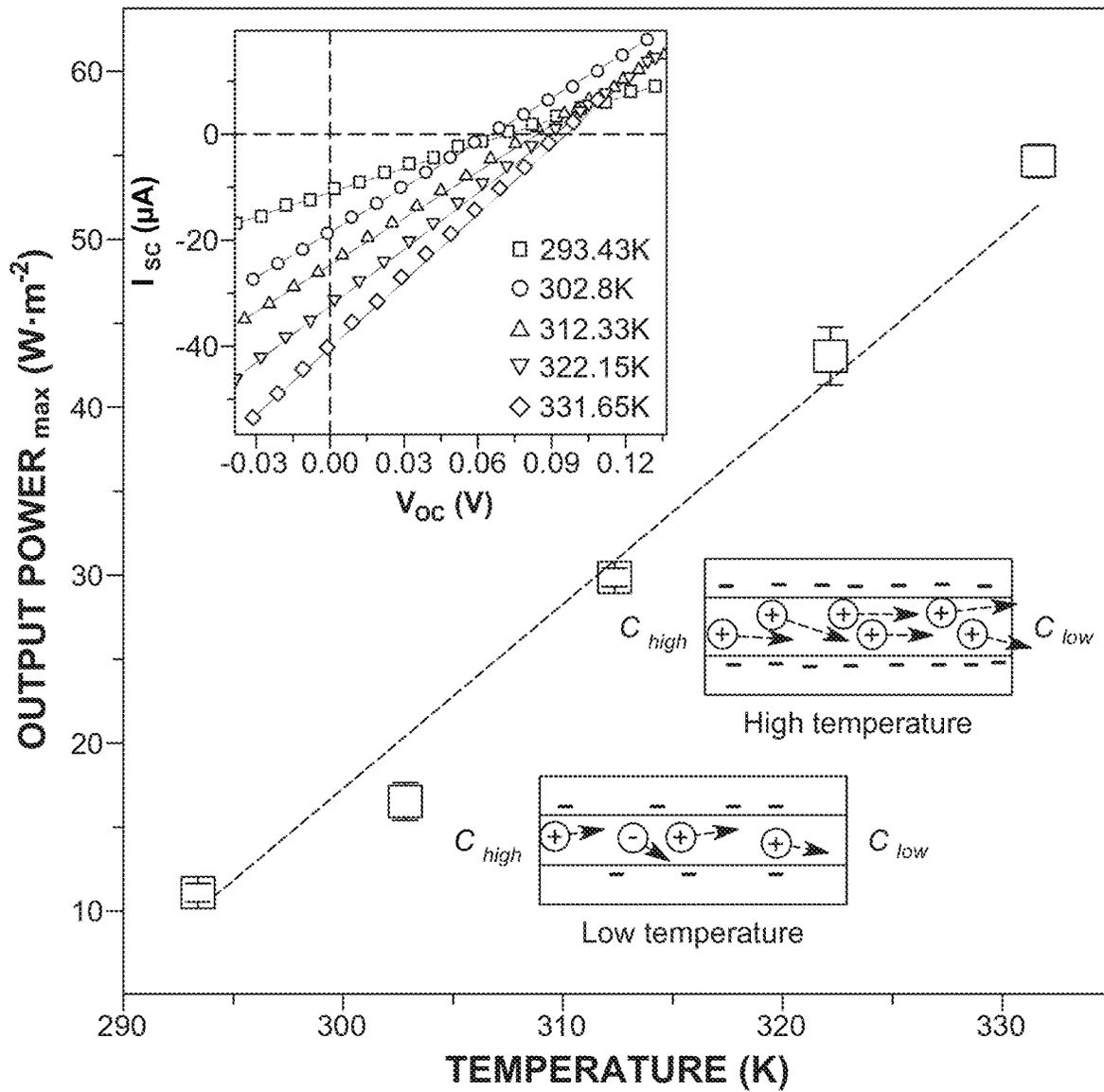


FIG. 7B

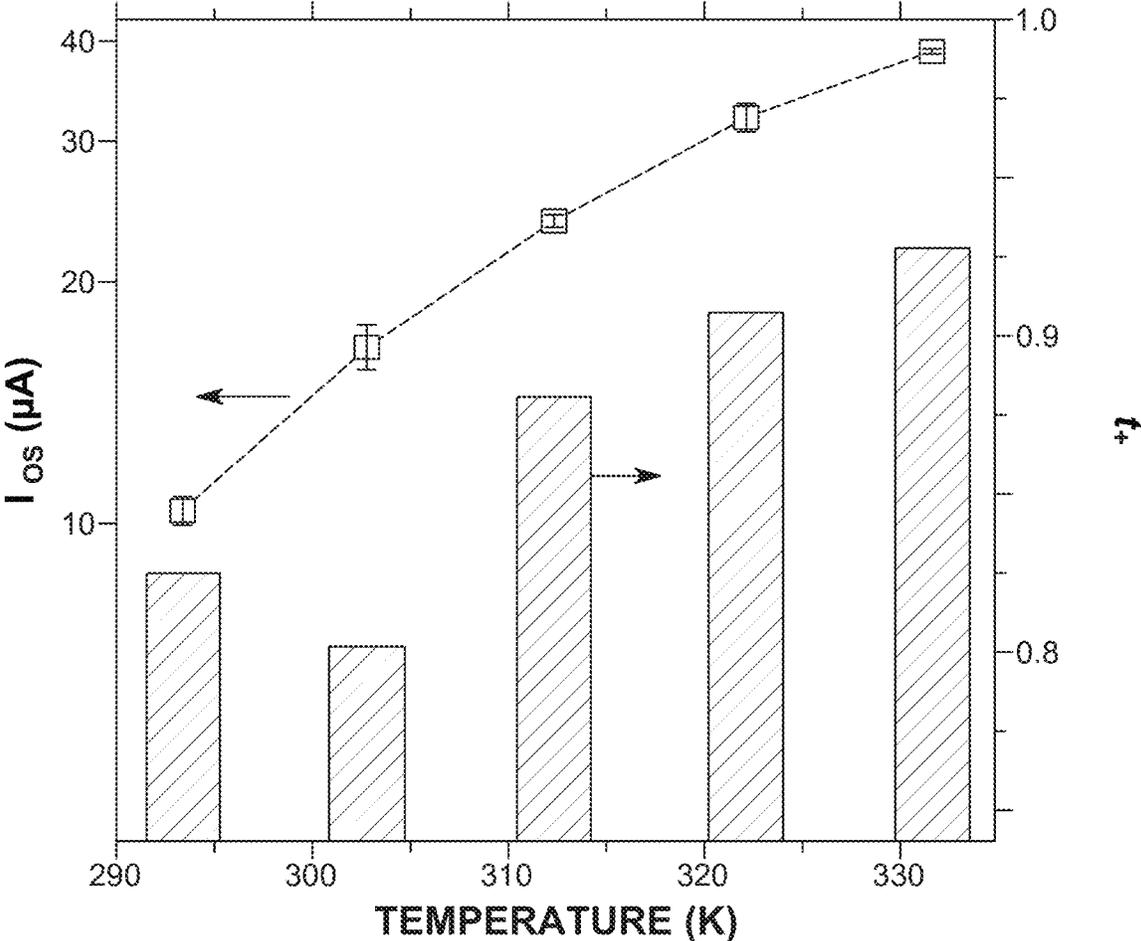


FIG. 7C

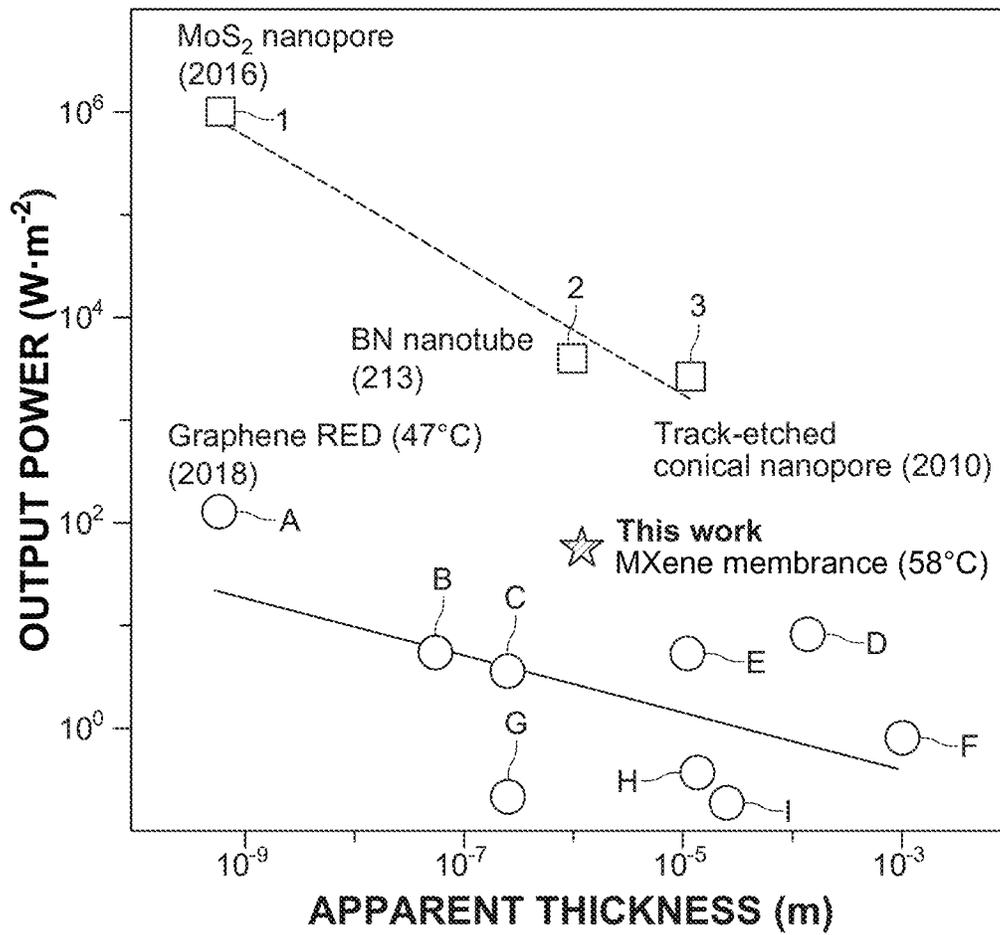


FIG. 7D

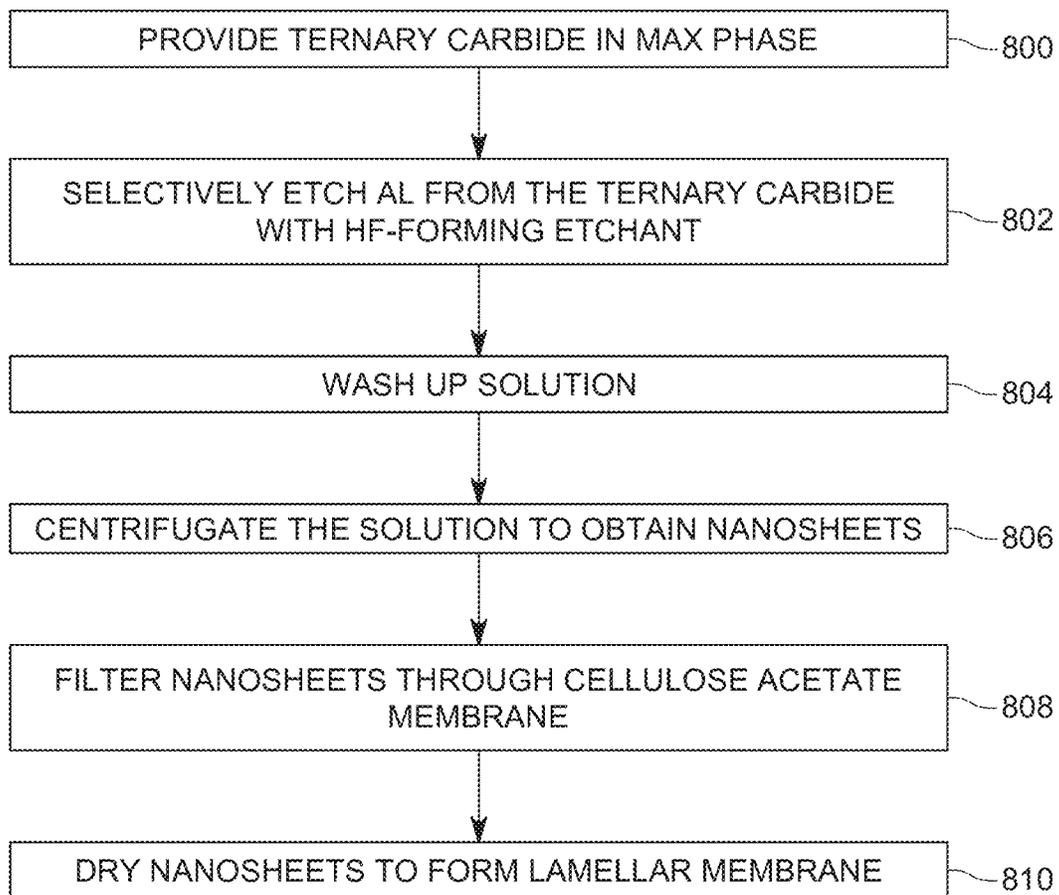


FIG. 8

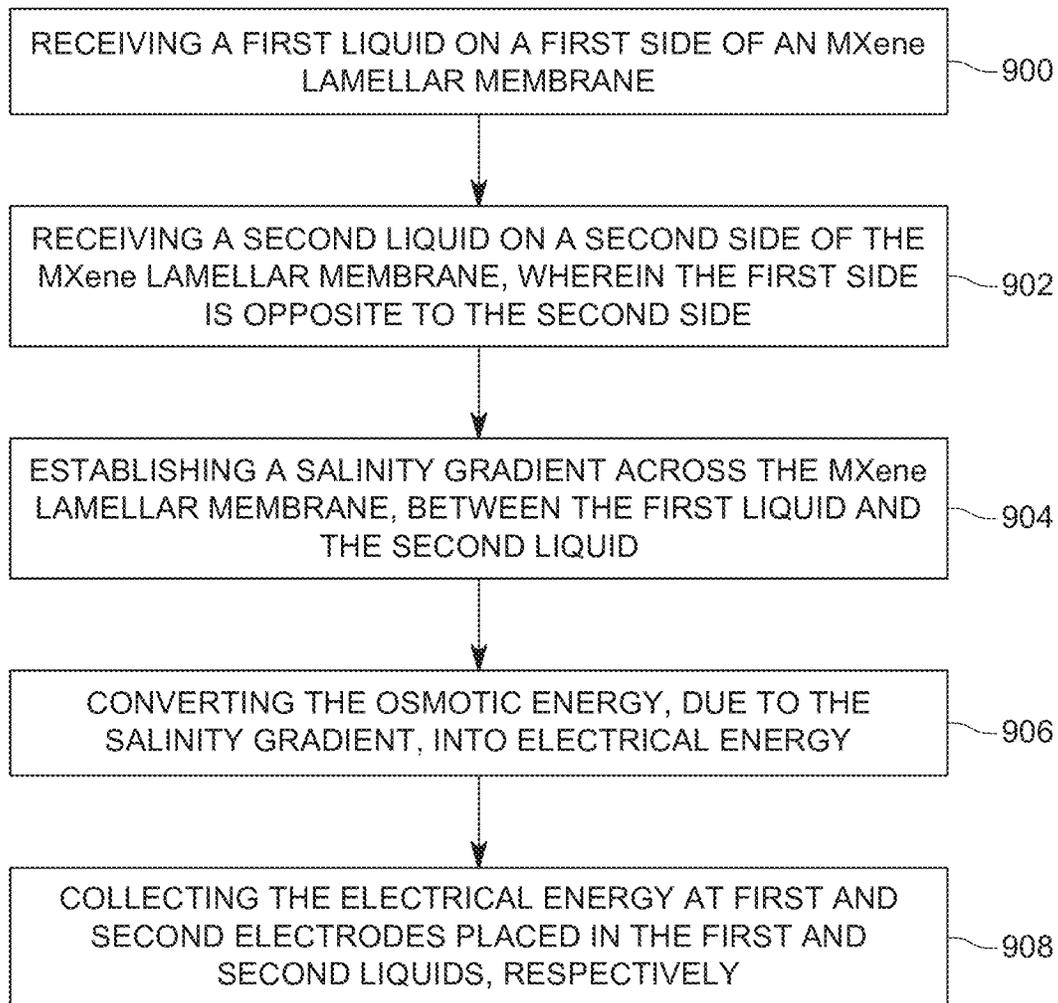


FIG. 9

# OSMOTIC ENERGY CONVERSION WITH MXENE LAMELLAR MEMBRANE-BASED SYSTEM AND METHOD

## BACKGROUND

### Technical Field

Embodiments of the subject matter disclosed herein generally relate to a system and method for using a salinity-gradient to generate electrical power, and more particularly, to using an MXene lamellar membrane having nanoconfined channels for converting the salinity-gradient into electrical power.

### Discussion of the Background

Salinity-gradient is in ubiquitous existence on Earth and has been extensively studied as a renewable and sustainable source of energy, popularly known as the blue energy. Salinity-gradient technologies generate electricity from the chemical pressure differential created by differences in ionic concentration between freshwater and seawater. Seawater has a higher osmotic pressure than freshwater due to its high concentration of salt. The extractable free energy of mixing of a concentrated salt solution with pure water is promising because the energy yield from this process is estimated to be 3 kJ per liter mixed, which is equivalent to  $0.8 \text{ kWhm}^{-3}$ .

To date, semipermeable, especially ion exchange, membranes have been explored for reverse electrodialysis (RED) to harness electricity from the Gibbs free energy of mixing under salinity gradient. Recently, nanoporous structures such as  $\text{MoS}_2$  nanopores and boron nitride nanotubes have been developed as a new class of RED membranes. Because of its size being close to the Debye screening length and its surface charges, the nanoconfined spacing in these nanostructures boosts the charge-selective osmotic current. However, despite their superior electricity generation performances, when compared to the conventional RED systems, the fabrication of these nanostructures is poorly scalable, which hinders their practical applications. In this regard, note that in order to be able to have an industrially suitable device that is capable to generate electricity from the salinity-gradient, the fabrication of the nanostructures used in this device should be available for large scale manufacturing, which is not yet the case for the existing devices.

Lamellar nanostructures, which can be fabricated by stacking two-dimensional (2D) nanosheets on top of each other, may provide a promising and scalable alternative to efficiently harvest the blue energy. Interplanar nanocapillaries between neighboring sheets are densely interconnected in the lamellar membranes and provide precise subnanometer fluidic channels that can facilitate ultrafast ion transport (see [1]-[7]). Equally importantly, the charges of the individual 2D nanosheet building blocks lead to surface-charge-governed ion transport behaviors within the lamellar membranes, which have been observed in graphene oxide- or carbon nitride-based lamellar membranes.

These membranes have outperformed their counterparts used in commercial RED systems [1], [3]. The simplicity and scalability of lamellar membrane fabrication makes it even more attractive for practical osmotic power generation. However, the membranes currently used for converting the osmotic energy still suffer from poor energy conversion and/or difficult manufacturing processes.

Thus, there is a need for a new lamellar membrane that solves the above noted problems and is capable to efficiently convert the osmotic energy into electrical energy.

## BRIEF SUMMARY OF THE INVENTION

According to an embodiment, there is an osmotic energy conversion system that includes a housing having a first inlet and a second inlet; an MXene lamellar membrane located inside the housing and configured to divide the housing into a first chamber and a second chamber; and first and second electrodes placed in the first and second chambers, respectively, and configured to collect electrical energy generated by a salinity-gradient formed by first and second liquids across the MXene lamellar membrane. The first chamber is configured to receive the first liquid at the first inlet and the second chamber is configured to receive the second liquid at the second inlet. The first liquid has a salinity lower than the second liquid, and the MXene lamellar membrane includes plural nanosheets of MXene stacked on top of each other.

According to another embodiment, there is a method for converting osmotic energy into electrical energy, and the method includes receiving a first liquid on a first side of an MXene lamellar membrane; receiving a second liquid on a second side of the MXene lamellar membrane, wherein the first side is opposite to the second side; establishing a salinity-gradient across the MXene lamellar membrane, between the first liquid and the second liquid; converting the osmotic energy, due to the salinity-gradient, into electrical energy; and collecting the electrical energy at first and second electrodes placed in the first and second liquids, respectively. The first liquid has a salinity lower than the second liquid, and the MXene lamellar membrane includes plural nanosheets of MXene stacked on top of each other.

According to still another embodiment, there is an osmotic energy conversion system that includes a housing; a  $\text{Ti}_3\text{C}_2\text{T}_x$  lamellar membrane located inside the housing; and first and second electrodes placed on opposite side of the  $\text{Ti}_3\text{C}_2\text{T}_x$  lamellar membrane, and configured to collect electrical energy generated by a salinity-gradient formed by first and second liquids across the  $\text{Ti}_3\text{C}_2\text{T}_x$  lamellar membrane. The first liquid has a salinity lower than the second liquid, and the  $\text{Ti}_3\text{C}_2\text{T}_x$  lamellar membrane includes plural nanosheets of  $\text{Ti}_3\text{C}_2\text{T}_x$  stacked on top of each other.

## BRIEF DESCRIPTION OF THE DRAWINGS

For a more complete understanding of the present invention, reference is now made to the following descriptions taken in conjunction with the accompanying drawings, in which:

FIG. 1 is a schematic diagram of an osmotic energy conversion system;

FIGS. 2A and 2B illustrate an MXene lamellar membrane for use in an osmotic energy conversion system;

FIGS. 3A and 3B illustrate a top surface and a cross-section, respectively, of the MXene lamellar membrane;

FIGS. 4A to 4C show the XRD patterns, XPS spectra, and Raman spectra of the MXene lamellar membrane;

FIG. 5A illustrates an osmotic energy conversion system, FIG. 5B illustrates the current-voltage characteristic for the system, FIG. 5C illustrates the conductance versus salinity of the system, and FIG. 5D illustrates the conductance and surface charge versus pH for the system of FIG. 5A;

FIG. 6A illustrates the current-voltage characteristic for a given gradient across the membrane, FIG. 6B illustrates the osmotic current and potential for various concentration

differences of the two fluids that wet the membrane, FIG. 6C illustrates the output power density versus the concentration difference of the two fluids of the osmotic energy conversion system, and FIG. 6D illustrates the output power density versus the thickness of the membrane;

FIG. 7A illustrates the ionic conductance at various temperatures in the system, FIG. 7B illustrates the maximum output power density as a function of temperature in the system, FIG. 7C illustrates the thermal dependence of the osmotic current, and FIG. 7D illustrates the output power density of the system versus the apparent thickness of the membrane;

FIG. 8 is a flowchart of a method for making the MXene lamellar membrane; and

FIG. 9 is a flowchart of a method for converting osmotic energy into electrical energy with the system shown in FIG. 1.

#### DETAILED DESCRIPTION OF THE INVENTION

The following description of the embodiments refers to the accompanying drawings. The same reference numbers in different drawings identify the same or similar elements. The following detailed description does not limit the invention. Instead, the scope of the invention is defined by the appended claims. The following embodiments are discussed, for simplicity, with regard to an osmotic energy conversion system that uses a lamellar membrane based on  $Ti_3C_2T_x$ . However, the embodiments to be discussed next are not limited to such material but may use other MXene nanosheets.

Reference throughout the specification to “one embodiment” or “an embodiment” means that a particular feature, structure or characteristic described in connection with an embodiment is included in at least one embodiment of the subject matter disclosed. Thus, the appearance of the phrases “in one embodiment” or “in an embodiment” in various places throughout the specification is not necessarily referring to the same embodiment. Further, the particular features, structures or characteristics may be combined in any suitable manner in one or more embodiments.

According to an embodiment, a novel osmotic energy conversion system includes an MXene lamellar membrane that separates a first high-saline medium from a second low-saline medium. The osmotic energy between the first and second mediums is converted into electrical energy.

Such a system 100 is illustrated in FIG. 1 and includes a housing 102 that is configured to receive the first low-salinity fluid 104 at a first inlet 102A, and the second high-salinity fluid 106, at a second inlet 102B. The first low-salinity fluid 104 may be fresh water and the second high-salinity fluid 106 may be seawater. In one application, both fluids 104 and 106 have a salinity, but the first fluid 104 has a salinity lower than the salinity of the second fluid 106. The first fluid 104 may be stored in a first storage container 110 while the second fluid 106 may be stored in a second storage container 112. In one embodiment, the first storage container 110 is a part of the ocean while the second storage container is a part of a river.

A lamellar membrane 120 is placed inside the housing 102 to separate a first chamber 122 from a second chamber 124. The first chamber 122 is fluidly connected to the first inlet 102A to receive the first fluid 104 and the second chamber 124 is fluidly connected to the second inlet 102B to receive the second fluid 106. In one application, the first chamber 122 has a first outlet 102C and the second chamber

124 has a second outlet 102D. The first fluid 104 may be discharged from the first chamber 122 into a first discharge storage tank 114, through the first outlet 102C, and the second fluid 106 may be discharged from the second chamber 124 into a second discharge storage tank 116, through the second outlet 102D. In one application, the first discharge storage tank is also the second discharge storage tank. Corresponding valves 114A and 116A may be located between the corresponding outlets and the discharge storage tanks to control an amount of fluid that is discharged from the chambers 122 and 124.

Two or more electrodes 130 and 132 are placed inside the housing 102, one in each of the chambers 122 and 124, and these electrodes are connected to an energy storage device 134. The electrodes may be placed directly into the first and second fluids. The energy storage device 134 may be a battery or similar device. The energy storage device 134 may be connected to a controller 136 and/or a motor 138. The controller 136 may include a processor, memory and communication means (e.g., receiver, transmitter, or transceiver) for exchanging data and/or commands with the various elements shown in FIG. 1, but also with a remote server (not shown). The controller 136 may be programmed to control the motor 138, based on the energy generated by the system 100, and also to control the movement of the fluids 104 and 106, from the storage tanks 110 and 112, through the housing 102, and into the discharge storage tanks 114 and 116. Motor 138 may be any device, for example, an engine, a turbine, etc.

The lamellar membrane 120 may be made from one or more materials. FIG. 2A shows an example of a lamellar membrane 120 that includes two-dimensional nanosheets 201, 202, 211, 212, 221, and 222 (only six of them are labeled for simplicity) disposed on top of each other to form plural layers I, II, III, etc. The 2D nanosheets may be made of metal carbide and nitride (MXene), which has recently joined the 2D materials family, and is emerging as a promising material to construct lamellar ion channels [7], [8]. MXene has typically a formula of  $M_{n+1}X_nT_x$  with  $n=1, 2,$  and 3, where M is an early transition metal and X is carbon and/or nitride, and is synthesized by selectively etching an A-group layer from the  $M_{n+1}AX_n$  phase, as discussed in [9] to [11]. The A-layer is replaced with surface terminal groups Tx, which may be Tx: —O, —OH, and —F, during an aqueous etching and exfoliation process. These functional groups endow the MXene nanosheets 201 to 222 with surface charges and help create interplanar spacing 209, 219 at subnanometer scale within the MXene nanosheets of the lamellar membrane 120.

In one embodiment, the lamellar membrane 120 is made of stacked  $Ti_3C_2T_x$  sheets 201 to 222, which are separated by an interlayer distance ( $d$ )~16.2 Å in a fully hydrated state. Taking into account that a theoretical thickness ( $a$ ) of a monolayer  $Ti_3C_2T_x$  sheet is about 9.8 Å, the empty space between two sheets in the same layer, which is available for ions to diffuse, is estimated to  $\delta=(d-a)$ ~6.4 Å. This effective interplanar spacing for ion transport is corresponding to the height of a nanocapillary. In one application, a thickness of a monolayer  $Ti_3C_2T_x$  sheet 201 is about 1 to 2 nm, and there are 1000 to 1500 monolayers in a lamellar membrane 120, so that a total thickness of the membrane 120 is between 100 nm and 3000 nm, with a preferred value of 400 nm. In one embodiment, the thickness of the membrane 120 is less than 3000 nm.

As shown in FIG. 2B, a full length of a single nanocapillary 250 with a thickness  $h$  involves a number of turns ( $h/d$ ), and each turn involves a capillary length ( $w$ ). In this

embodiment, it is assumed that the single  $\text{Ti}_3\text{C}_2\text{T}_x$  sheet **201** possesses a same width and length  $w$ , and those are approximated from experimentally averaged lateral sizes to be about  $3.4 \mu\text{m}$  of the MXene sheets. Therefore, the complete length of the single nanocapillary **250** is given by  $w \times h/d$ . The total number of parallel 2D channels **209** and **219** per unit area can be estimated to be about  $1/w^2$ , and a resulting number of channels is about  $10^7$  across an employed membranes with a full area of  $0.196 \text{ cm}^2$ . The effective areal fraction of the nanocapillaries on the total membrane area is estimated to be approximately 0.1%.

Thus, the scalable MXene lamellar membrane **120** may be used as a nanofluidic platform to harness the salinity-gradient energy. The subnanometer channels **209**, **219** in the MXene membrane **120** exhibit strong surface-charge-governed ion transport and consequentially excellent osmotic energy conversion efficiency up to 40.6% at room temperature. The thermal-dependent osmotic energy conversion is discussed later at elevated temperature, giving rise to an electricity generation of  $54 \text{ W} \cdot \text{m}^{-2}$  at 331 K. These performances all transcend the state-of-the-art RED devices. These results indicate the practical feasibility and viability of the MXene laminar membranes as a large-scale osmotic energy-harvesting platform.

The  $\text{Ti}_3\text{C}_2\text{T}_x$  nanosheet **201** was synthesized in one embodiment by selective etching the Al from the MAX phase  $\text{Ti}_3\text{AlC}_2$  using in situ HF-forming etchant. A transmission electron microscopic (TEM) image of the exfoliated  $\text{Ti}_3\text{C}_2\text{T}_x$  nanosheets clearly shows (see FIG. **3A**) well defined edges **300** as well as plain surfaces **302** with no wrinkles. Its high crystallinity with no obvious defects and hexagonal structure is also confirmed by the high-resolution TEM image and selected area electron diffraction (SAED) pattern. An atomic force microscopic (AFM) measurement indicates that the exfoliated monolayer  $\text{Ti}_3\text{C}_2\text{T}_x$  nanosheet possesses a thickness of  $\sim 1.5 \text{ nm}$ . The average lateral size of the generated nanosheets is approximately  $4.2 \pm 1.8 \mu\text{m}$  and  $2.6 \pm 1.1 \mu\text{m}$  in length and width, respectively. Additionally, the high aspect ratio (micrometer lateral width to nanometer thickness) of MXene sheets is a favorable feature for creating uniform 2D interlayer channels in a well-aligned stacked manner.

The 2D lamellar nanosheets **201** to **222** were assembled by vacuum assisted filtration of  $\text{Ti}_3\text{C}_2\text{T}_x$  dispersion on porous polymeric support, to form the lamellar membrane **120**. The stacked nanosheets can be easily peeled off from the support without damage after drying in air, leading to free-standing flexible MXene membranes. The SEM image (see FIG. **3B**) displays highly oriented MXene nanosheets **201**, **212**, parallel to a support surface **310**. Additionally, the insert of FIG. **3B** indicates that, at the macroscopic level, the laminate membrane **120** has an outer smooth surface with no detectable pinholes or cracks. The thickness of the membrane **120** is controlled by the mass of MXene in the filtrating dispersion.

The ordered stacked structure **120** is further characterized by X-ray diffraction (XRD). The results of this analysis are shown in FIG. **4A**, which indicate a pronounced (002) peak **402** in the X-ray diffraction pattern **400** of the  $\text{Ti}_3\text{C}_2\text{T}_x$  membrane when compared to the peak **404** of the XRD pattern **406** of the  $\text{Ti}_3\text{AlC}_2$  material. Note the shift of the (002) peak **402** of the  $\text{Ti}_3\text{C}_2\text{T}_x$  material to a lower angle than the  $9.6^\circ$  value for the peak **404** of the MAX phase, which indicates the introduction of the functional groups  $\text{T}_x$  and water in between adjacent MXene nanosheets. Also note that

the shift in the (002) peak for the  $\text{Ti}_3\text{C}_2\text{T}_x$  material when exposed to ambient **403** or in water **405**, as illustrated in the inset of FIG. **4A**.

The surface functional groups of the  $\text{Ti}_3\text{C}_2\text{T}_x$  nanosheets are examined by X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy as shown in FIGS. **4B** and **4C**. The XPS spectra **420** in FIG. **4B** show that abundant surface terminal groups, including  $-\text{O}$ ,  $-\text{OH}$ , and  $-\text{F}$ , are bonded to the surface of the  $\text{Ti}_3\text{C}_2$  sheets. These functional groups, evidenced by the Raman spectra **430** in FIG. **4C** as well, ensure that the MXene lamellar membrane **120** is hydrophilic and negatively charged.

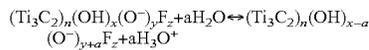
In a hydrated state, these terminal functional groups, which act as spacers to keep neighboring nanosheets apart, allow water molecules to be intercalated inside the interplanar channels **209** and **219** while preventing the laminates **201** to **222** from being disintegrated. The enlarged channel height is verified by the shift of the (002) peak to  $2\theta = 5.46^\circ$  in its XRD pattern in the inset of FIG. **4A**, corresponding to an interlayer spacing of  $1.615 \text{ nm}$ . The effective interplanar nanocapillary is estimated to be about  $0.64 \text{ nm}$ , which is large enough for hydrated small ions to diffuse. For instance, the reported diameter of hydrated  $\text{K}^+$  varies from  $0.4$  to  $0.66 \text{ nm}$ . Additionally, the lamellar structure of the MXene membrane **120** is stable in water under all experimental conditions employed, showing its high aqueous stability [7].

To determine the intrinsic ionic transport properties of the MXene membrane **120**, a current-voltage (I-V) response for the  $\text{Ti}_3\text{C}_2\text{T}_x$  lamellar membrane under various salt (e.g., KCl) concentrations and pH values was measured. These measurements provide information about the surface charges of the  $\text{Ti}_3\text{C}_2\text{T}_x$  nanochannels. Unless otherwise mentioned, all ion transport experiments were carried out with a membrane having a thickness of  $2.7$  to  $3.0 \mu\text{m}$ . The approximated length of a single nanocapillary **250** is derived from the thickness of the membrane, and the width is approximated to be the averaged lateral sizes ( $\sim 3.4 \mu\text{m}$ ) of the MXene nanosheets illustrated in FIG. **2A** [4], [6]. The electric current passing through the MXene membrane **120** was measured by using a pair of Ag/AgCl electrodes **130**, **132**, with  $10 \text{ pA}$  precision, as illustrated in FIG. **5A**. A sourcemeter **500** was connected to the two electrodes to measure the voltage and corresponding current in this electrical circuit. Note that the positive ions **502** move through the membrane **120** along the arrow **504**, due to the salinity-gradient between the first low-salinity fluid **104** and the second high-salinity fluid **106**. The salinity of the two fluids is indicated by the symbol "C" in FIG. **5A**.

FIG. **5B** shows representative I-V characteristics for a range of KCl concentrations ( $10^{-1}$  to  $10^{-3} \text{ M}$  in the figure, where M stands for mol per liter) at pH 5.7. The Ohmic conductance  $G$  of the MXene membrane **120** at smaller biases ( $< 30 \text{ mV}$ ), where the I-V curve is linear, is plotted in FIG. **5C** as a function of the salt concentration at pH 5.7. The linear response **510**, which is typical of charge-neutral channels, at  $1 \text{ M}$  agrees well with the bulk conductivity **512** of the KCl solution for the given channel geometry. However, starting from  $100 \text{ mM}$ , the conductance  $G$  deviates from the linear regime **512**, implying the presence of surface charges in the interplanar space. The surface charge effect was previously reported to dominate at low salt concentrations through nanoconfined channels. Particularly, overlapped electrical double layers in nanochannels, derived from slit size close to Debye screening length as well as surface charges explain the observation of the higher-than-bulk ionic conductance **514**.

Furthermore, a scaling behavior is observed at low salt concentration. It is believed that salinity-dependent surface charges may be responsible for such monotonic decrease in conductance, which was previously predicted by the chemical equilibrium model in the SiO<sub>2</sub> nanochannel or nanopore. From the measured conductance *G* for KCl 10 mM at pH 6.3, it was found that the surface charge density is as high as 100 mC·m<sup>-2</sup>, which is higher than the values for graphene oxide laminate (50-60 mC·m<sup>-2</sup>) as well as the values for perforated graphene (~40 mC·m<sup>-2</sup>) or MoS<sub>2</sub> nanopores (20-80 mC·m<sup>-2</sup>) at pH 5.

In addition, the surface terminal groups are randomly distributed in the basal planes of the MXene sheets. It was noted that this property plays a key role in the highly cation-selective ion flow through the MXene nanochannels. The conductance of the membrane **120** can be further modulated by controlling the pH as shown in FIG. 5D. The conductance *G* gradually increases with increasing the pH value above 6, suggesting more accumulation of negative surface charges in the MXene nanosheets at higher pH. The estimated charge density above pH 9 reaches up to ~130 mC·m<sup>-2</sup>, corresponding to 0.84e nm<sup>-2</sup>. When the pH is increased, the dissociation of the terminal groups leads to more negative surface charges on the individual MXene nanosheets, following a chemical equilibrium as:



Zeta potential (the zeta potential measurement is a technique for determining the surface charge of nanoparticles in a colloidal solution) values obtained from colloidal nanosheets and stacked membranes indicate the strong dependence of the surface charges of the Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> membrane on the pH, see inset of FIG. 5D. In contrast, the conductance *G* sharply declines at a pH <6. This can be associated with fewer counterions inside channels and narrowed interlayer spacing due to the protonation of the surface functional groups.

To study the influence of the chemical gradient across the lamellar membrane **120**, different KCl concentrations are tested, for example, in the range of 1 mM to 1 M in the two chambers **122** and **124**. Charge separation by interplanar channels **209**, **219** is responsible for harvesting the electrical energy from the chemical potential gradient. The selective passage of the cations **502** from high to low concentrations, whereas the transport of the anions **506** is electrostatically impeded, as illustrated in FIG. 5A, results in a positive net current across the lamellar membrane **120**. In this regard, FIG. 6A illustrates a current-voltage response **600** under a variable concentration gradient, which is defined as the ratio  $c_{high}/c_{low}$ . A direction of the short circuit current (*I<sub>sc</sub>*) in the absence of bias is consistent with a net flow of positive charges, and this charge-selective osmotic flow produces an open circuit voltage (*V<sub>oc</sub>*) across the lamellar membrane **120**. Note that the inset of FIG. 6A illustrates the electrical diagram associated with the osmotic energy conversion system **100**. The pure electroosmotic current-voltage **602** can then be calculated from the osmotic current (*I<sub>os</sub>*) and potential (*V<sub>os</sub>*), corrected for redox potentials (*V<sub>redox</sub>*) emanating from unequal potential drops at the electrode-solution interfaces in different salt concentration. More specifically, the redox potential is calculated using the Nernst equation in combination with the Pitzer model, taking into account a temperature-dependent ion activity coefficient. FIG. 6B shows the osmotic potential and current obtained for different salt concentration gradient and pH conditions.

The osmotic potential is increased from 28 to 139 mV at pH 11.53 with varying the gradients from 10-fold to 1000-fold. The osmotic current reaches up to 14.2 μA at a higher pH under the gradient of 100. A slight current drop is also observed under the gradient of 1000, which is likely due to relatively stronger ion concentration polarization effect at the surface of membranes. Calculated by the equation:  $t_+ = 0.5(1 + V_{os}/V_{redox})$ , the cation transference number (*t<sub>+</sub>*) approaches 0.95 under 1000-fold difference and highly alkaline conditions, nearly close to ideal unity cation selectivity. Note that the transference number is defined as the fraction of the current carried either by the anion (*J<sub>-</sub>*) or the cation (*J<sub>+</sub>*) to the total electric current (i.e.,  $t_+ = J_+/(J_+ + J_-)$ ). A significant increase in the osmotic current and voltage is observed at a higher pH, implying that the surface charge plays a critical role in the osmotic power generation process.

Based on the estimated *I<sub>os</sub>* and *V<sub>os</sub>* from the curve **602**, a maximum output power density (*PD<sub>max</sub>*) **610** and its corresponding electrochemical energy conversion efficiency (*η<sub>max</sub>*) **612** were calculated and plotted in FIG. 6C. The *PD<sub>max</sub>* **610** reaches up to 20.85 W·m<sup>-2</sup> which is higher by a factor of around 20 than those from the existing commercial ion exchange membranes, and the *η<sub>max</sub>* **612** is as high as 40.6% at a pH value of 11.5 for the salinity gradient of 1000, as shown in FIG. 6C. Note that in this figure, the *PD<sub>max</sub>* is represented on the Y axis, on the left hand side of the graph while the electrochemical energy conversion efficiency *η<sub>max</sub>* is also represented on the Y axis, but on the right hand side of the graph. The MXene membrane **120** shows a higher output power by 2 orders of magnitude, compared to other 2D materials such as graphene oxide or carbon nitride. Such an enhancement of the MXene membranes could be associated with their lower membrane resistance through the structurally regular and straight Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> nanocapillaries, contrasting to conventional irregular ones from other lamellar membranes.

The inventors have found that the osmotic energy conversion depends on the thickness of laminar membrane under ambient pH conditions. The power density exhibits a strong decay with increasing membrane thickness, as illustrated in FIG. 6D. Above a certain thickness, a longer channel length derived from a thicker membrane is found to impair the ionic flux. This implies that further enhancement of the osmotic power density can be achieved by reducing the nanocapillary length of the membrane. It was observed that the longitudinal length of the nanocapillaries in several nanometer-thick layered membranes can be coincident with the characteristic length scale (400-1000 nm) of the optimum nanofluidic channels, to maximize the power generation while balancing the energy conversion efficiency. Under these conditions, an excellent performance may ideally occur in an ultrathin Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> laminar membrane at several nanometer scale. From a technical perspective, emerging techniques such as a roll-to-roll process, beneficial for a controlled large-scale 2D sheet assembly, may be used to realize the uniform deposition of such ultrathin membranes.

To improve the osmotic energy conversion performance, the inventors have studied the thermal effect on the ionic transport and its consequential impact on the power generation effect. As shown in FIG. 7A, the ionic conductance *G* at a temperature in the range of 294 to 341 K shows a linear dependence **700** on the temperature and furthermore follows the Arrhenius behavior. As previously demonstrated for a silica nanopore array, the fluid temperature can affect not only the surface charge and chemistry, but also the properties of the liquid media such as viscosity. As the temperature

of the membrane's ambient rises, the ionic mobility increases by a factor of 2.35 in response to a reduced water viscosity.

The estimated mobility enhancement is fairly consistent with the observed increase in the conductance. As expected, the output power shows a strong thermal dependence, reaching up to  $54 \text{ W}\cdot\text{m}^{-2}$  at 331 K, as shown in FIG. 7B. Note that FIG. 7B shows the maximum output power density as a function of temperature, under a KCl concentration gradient of 100 at a pH value of 5.7. The inset in FIG. 7B shows representative I-V characteristics at different temperatures. Further, the inventors found that the thermal effect increases the surface charge as well, which is evidenced by the incremental cation transference number shown in FIG. 7C (see Y axis, right hand side of the figure). An ionic clogging, possibly arising from bubble nucleation in the capillaries, was not observed at elevated temperatures.

Accordingly, the temperature-dependent enhancement of the output power is an understandable result of the increase in local concentration and mobility of cations on the charged surfaces. Besides, the lamellar membrane **120** sustained its stable chemical feature as well as mechanical integrity even after a temperature rise. It should be noted that this thermal performance is promising from a practical perspective, because widely available industrial waste heat can be tapped into for further enhancing the osmotic power generation. When comparing the osmotic energy conversion system **100** with other power generators, as illustrated in FIG. 7D, the resultant output power of the MXene  $\text{Ti}_3\text{C}_2\text{T}_x$  lamellar membrane **120** at high temperature is higher than the performances of state-of-the-art osmotic power generators. FIG. 7D includes labels B to I, which correspond to the following existing membranes: B is the mesoporous silica film (2017), C is the Janus Carbon/alumina membrane (2014), D is Silica nanochannels (2010), E is Janus 3D porous membrane (2018), F is Nafion-filled PDMS microchannels (2016), G is polymeric carbon nitride laminate (2018), H is BCP-coated PET conical nanochannels (2015), and I is Janus nanokaolinite film (2017).

Furthermore, the inventors found that the osmotic power performance of the system **100** can be stably maintained for more than 20 h, even with  $\text{Na}^+$ , the most abundant ion of seawater. Based on these observations, the system **100** shown in FIG. 1 may be configured to have a heating element **170** to heat one of the first and second fluids. In one application, the heating element **170** is a solar cell. In another application, the heating element **170** is a heat exchanger that takes heat from industrial waste heat and transfers it to one or both of the first and second fluids. The amount of heat transferred from the heating element **170** to the first and/or second fluids is controlled by controller **136**.

A method for forming the MXene lamellar membrane **120** is now discussed with regard to FIG. 8. The method starts in step **800** with providing layered ternary carbide  $\text{Ti}_3\text{AlC}_2$  (MAX phase) powder, that is commercially procured (e.g., having particle size  $<40 \mu\text{m}$ ). In step **802**,  $\text{Ti}_3\text{C}_2\text{T}_x$  MXene is synthesized by selective etching of the Al from the  $\text{Ti}_3\text{AlC}_2$  powder using in situ HF-forming etchant. The etching solution was prepared by adding 1 g of lithium fluoride to 20 mL of hydrochloric acid (HCl 35-38%) followed by stirring for 5 min. Then, 1 g of  $\text{Ti}_3\text{AlC}_2$  powder was slowly added to the above etchant at  $35^\circ \text{C}$ . and stirred for 24 h. The acidic suspension was washed in step **804** with deionized water using centrifugation at 3,500 rpm for 5 min per cycle, and the centrifugal washing of a supernatant collected after each cycle was repeated until pH  $>6$ . At around pH 6, a stable dark green supernatant of  $\text{Ti}_3\text{C}_2\text{T}_x$  was

observed, and then a final supernatant was collected at step **806** by additional centrifugation at 3,500 rpm for 5 min. The lamellar MXene  $\text{Ti}_3\text{C}_2\text{T}_x$  membrane **120** was fabricated by filtering in step **808** specific amounts of MXene dispersion through a cellulose acetate membrane (0.45  $\mu\text{m}$  pore size and a diameter of 43 mm). All filtrated membranes were air-dried in step **810**, at ambient conditions, and could be easily detached from the support.

A method for converting osmotic energy into electrical energy with the lamellar membrane discussed above is now presented with regard to FIG. 9. The method includes a step **900** of receiving a first liquid **104** on a first side of an MXene lamellar membrane **120**, a step **902** of receiving a second liquid **106** on a second side of the MXene lamellar membrane **120**, where the first side is opposite to the second side, a step **904** of establishing a salinity gradient across the MXene lamellar membrane **120**, between the first liquid and the second liquid, a step **906** of converting the osmotic energy, due to the salinity gradient, into electrical energy, and a step **908** collecting the electrical energy at first and second electrodes **130**, **132** placed in the first and second liquids, respectively. The first liquid has a salinity lower than the second liquid and the MXene lamellar membrane includes plural nanosheets of MXene stacked on top of each other.

In one embodiment, a thickness of the MXene lamellar membrane is less than 3000 nm. In another embodiment, the thickness of the MXene lamellar membrane is 400 nm. The MXene lamellar membrane includes between 1000 and 1500 nanosheets of MXene and the MXene includes  $\text{Ti}_3\text{C}_2\text{T}_x$  sheets, wherein  $\text{T}_x$  includes O and OH and F. The MXene lamellar membrane has nanoconduits between adjacent nanosheets, the first fluid is seawater and the second fluid is freshwater. In one application, the method may include a step of heating the first liquid.

The disclosed embodiments provide an osmotic energy conversion system that transform osmotic energy into electrical energy. It should be understood that this description is not intended to limit the invention. On the contrary, the embodiments are intended to cover alternatives, modifications and equivalents, which are included in the spirit and scope of the invention as defined by the appended claims. Further, in the detailed description of the embodiments, numerous specific details are set forth in order to provide a comprehensive understanding of the claimed invention. However, one skilled in the art would understand that various embodiments may be practiced without such specific details.

Although the features and elements of the present embodiments are described in the embodiments in particular combinations, each feature or element can be used alone without the other features and elements of the embodiments or in various combinations with or without other features and elements disclosed herein.

This written description uses examples of the subject matter disclosed to enable any person skilled in the art to practice the same, including making and using any devices or systems and performing any incorporated methods. The patentable scope of the subject matter is defined by the claims, and may include other examples that occur to those skilled in the art. Such other examples are intended to be within the scope of the claims.

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What is claimed is:

1. An osmotic energy conversion system comprising:  
 a housing having a first inlet and a second inlet;  
 an MXene lamellar membrane located inside the housing  
 and configured to divide the housing into a first chamber  
 and a second chamber; and  
 first and second electrodes placed in the first and second  
 chambers, respectively, and configured to collect electrical  
 energy generated by a salinity-gradient formed by  
 first and second liquids across the MXene lamellar  
 membrane,  
 wherein the first chamber is configured to receive the first  
 liquid at the first inlet and the second chamber is  
 configured to receive the second liquid at the second  
 inlet,  
 wherein the first liquid has a salinity lower than the  
 second liquid, and  
 wherein the MXene lamellar membrane includes plural  
 nanosheets of MXene stacked on top of each other, the  
 plural nanosheets of MXene forming a nanocapillary  
 that extends from one side of the MXene lamellar

- membrane to an opposite side, and a full length of the  
 nanocapillary is between 400 and 1000 nm.
2. The system of claim 1, wherein a thickness of the  
 MXene lamellar membrane is less than 3,000 nm.
3. The system of claim 1, wherein a thickness of the  
 MXene lamellar membrane is 400 nm.
4. The system of claim 1, wherein the MXene lamellar  
 membrane includes between 1,000 and 1,500 layers of  
 nanosheets of MXene.
5. The system of claim 1, wherein the MXene includes  
 Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> sheets.
6. The system of claim 5, wherein T<sub>x</sub> includes O and OH  
 and F.
7. The system of claim 1, wherein the MXene lamellar  
 membrane has nanoconduits between adjacent nanosheets.
8. The system of claim 1, wherein the first liquid is  
 freshwater and the second liquid is seawater.
9. The system of claim 1, further comprising:  
 a heating element configured to heat the first liquid.
10. A method for converting osmotic energy into electrical  
 energy, the method comprising:  
 receiving a first liquid on a first side of an MXene lamellar  
 membrane;  
 receiving a second liquid on a second side of the MXene  
 lamellar membrane, wherein the first side is opposite to  
 the second side;  
 establishing a salinity-gradient across the MXene lamellar  
 membrane, between the first liquid and the second  
 liquid;  
 converting the osmotic energy, due to the salinity-gradi-  
 ent, into electrical energy; and  
 collecting the electrical energy at first and second elec-  
 trodes placed in the first and second liquids, respec-  
 tively,  
 wherein the first liquid has a salinity lower than the  
 second liquid, and  
 wherein the MXene lamellar membrane includes plural  
 nanosheets of MXene stacked on top of each other, the  
 plural nanosheets of MXene form a nanocapillary that  
 extends from one side of the MXene lamellar mem-  
 brane to an opposite side, and a full length of the  
 nanocapillary is between 400 and 1000 nm.
11. The method of claim 10, wherein a thickness of the  
 MXene lamellar membrane is less than 3,000 nm.
12. The method of claim 10, wherein a thickness of the  
 MXene lamellar membrane is 400 nm.
13. The method of claim 10, wherein the MXene lamellar  
 membrane includes between 1,000 and 1,500 layers of  
 nanosheets of MXene.
14. The method of claim 10, wherein the MXene includes  
 Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> sheets.
15. The method of claim 14, wherein T<sub>x</sub> includes O and  
 OH and F.
16. The method of claim 10, wherein the MXene lamellar  
 membrane has nanoconduits between adjacent nanosheets.
17. The method of claim 16, wherein the first liquid is  
 freshwater and the second liquid is seawater.
18. The method of claim 10, further comprising:  
 heating the first liquid.
19. An osmotic energy conversion system comprising:  
 a housing;  
 a Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> lamellar membrane located inside the housing;  
 and  
 first and second electrodes placed on opposite side of the  
 Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> lamellar membrane, and configured to collect

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electrical energy generated by a salinity-gradient formed by first and second liquids across the  $Ti_3C_2T_x$  lamellar membrane,

wherein the first liquid has a salinity lower than the second liquid, and

wherein the  $Ti_3C_2T_x$  lamellar membrane includes plural nanosheets of  $Ti_3C_2T_x$  stacked on top of each other, the plural nanosheets of  $Ti_3C_2T_x$  forming a nanocapillary that extends from one side of the  $Ti_3C_2T_x$  lamellar membrane to an opposite side, and a full length of the nanocapillary is between 400 and 1000 nm.

**20.** The system of claim **19**, wherein a thickness of the  $Ti_3C_2T_x$  lamellar membrane is 400 nm and the  $Ti_3C_2T_x$  lamellar membrane includes between 1,000 and 1,500 layers of nanosheets of  $Ti_3C_2T_x$ .

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